



Review

A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis

Quan Bu^a, Hanwu Lei^{a,*}, Alan H. Zacher^b, Lu Wang^a, Shoujie Ren^a, Jing Liang^a, Yi Wei^a, Yupeng Liu^a, Juming Tang^a, Qin Zhang^a, Roger Ruan^c

^a Bioproducts, Sciences and Engineering Laboratory, Department of Biological Systems Engineering, Washington State University, Richland, WA 99354-1671, USA

^b Pacific Northwest National Laboratory, Richland, WA 99354-1671, USA

^c Department of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, MN 55108, USA

HIGHLIGHTS

- First review of the catalytic hydrodeoxygenation (HDO) of lignin-derived phenols.
- Review of the applied HDO catalysts.
- Review of reaction mechanism of HDO of lignin-derived phenols.
- Review of the kinetics of HDO of different lignin-derived model compounds.
- HDO-prospects and required further research and developments are discussed.

ARTICLE INFO

Article history:

Received 10 July 2012

Received in revised form 21 August 2012

Accepted 22 August 2012

Available online 30 August 2012

Keywords:

Lignin-derived phenols

Catalytic hydrodeoxygenation (HDO)

Pyrolysis

Mechanism

Kinetics

ABSTRACT

Catalytic hydrodeoxygenation (HDO) of lignin-derived phenols which are the lowest reactive chemical compounds in biomass pyrolysis oils has been reviewed. The hydrodeoxygenation (HDO) catalysts have been discussed including traditional HDO catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts and transition metal catalysts (noble metals). The mechanism of HDO of lignin-derived phenols was analyzed on the basis of different model compounds. The kinetics of HDO of different lignin-derived model compounds has been investigated. The diversity of bio-oils leads to the complexities of HDO kinetics. The techno-economic analysis indicates that a series of major technical and economical efforts still have to be investigated in details before scaling up the HDO of lignin-derived phenols in existed refinery infrastructure. Examples of future investigation of HDO include significant challenges of improving catalysts and optimum operation conditions, further understanding of kinetics of complex bio-oils, and the availability of sustainable and cost-effective hydrogen source.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Progressive depletion of petroleum-based fuels has led to the global energy crisis. The greenhouse gas (GHG) emission introduced by burning fossil fuels has made the global warming become one of the biggest environmental challenges in human history (Nigam and Singh, 2010). As one of the most significant renewable resources on earth and the only renewable resource to be converted to liquid fuel, biomass has recently received considerable attentions when people search for alternatives of fossil fuel (Rocha et al., 1996; Tang et al., 2009). The major components of biomass are cellulose, hemicellulose and lignin. Cellulose and hemicellulose are consisted of complex polysaccharides (White et al., 2011).

Lignins are highly substituted and mononuclear phenolic amorphous polymers consisting of phenylpropane units, the precursors of which are three monolignols including p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Buranov and Mazza, 2008; Freudenberg and Nash, 1969; Kuroda, 2000; Yaman, 2004). Cellulosic biomass can be converted into transportation fuels by three major pathways: syngas production by gasification, bio-oils production by pyrolysis or liquefaction, and aqueous sugar by hydrolysis (Huber et al., 2006). However, these are the initial steps in the pathways towards transportation fuels; products upgrading/separation is often more extensive than the primary conversions of biomass.

Pyrolysis of biomass is a thermal decomposition process of organic compounds in the absence of oxygen to obtain char, syngas, and bio-oil. The bio-oil yield from fast pyrolysis is up to 60–70 wt.% which contains 15–30 wt.% of water (Brems et al., 2011; Velden

* Corresponding author. Tel.: +1 509 372 7628; fax: +1 509 372 7690.

E-mail address: hlei@tricity.wsu.edu (H. Lei).

et al., 2008, 2010). Currently, bio-oil is considered as an alternative to petroleum-based sources for a wide range of fuels and high value-added chemicals and other products (Yaman, 2004; Brems et al., 2011). Bio-oil can be used as a liquid fuel or for the production of chemicals and high grade transportation fuels after upgrading and separation. Potential bio-based chemicals from bio-oil include phenolics (Bu et al., 2012; Ren et al., 2012) and cyclic ketones for resins and solvents, levoglucosan and levoglucosenon for polymers, and aromatic hydrocarbons for fuels and solvents (Elliot, 2004; Maher and Bressler, 2007).

With the development of lignocellulose-to-ethanol process and lignin waste from pulp and paper refineries, recently a broad interest to make full use of lignin for production of renewable fuels and chemicals was developed. Fast pyrolysis oil from lignocellulosic materials is known to contain a complex mixture of phenolic compounds which are the products primarily derived from the lignin fractionation of the biomass. Lignins are much more thermally stable than cellulose and hemicellulose during biomass pyrolysis (Bridgwater, 1999). The compounds obtained from decomposition of lignin have become one of the biggest challenges during upgrading of bio-oils. Although there were a massive increasing interest in biofuels production by bio-oil upgrading and the utilization of lignin which is abundant from lignocellulose-to-ethanol process and pulp and paper refineries (Adjaye and Bakhshi, 1995; Sharma and Bakhshi, 1991; Chen et al., 2001; Mukkamala et al., 2012; Kleinert and Barth, 2008; DeWild et al., 2009), there are just few major reviews referring to the production of chemicals from lignin-derived monomeric phenols via catalytic hydrotreatment (Pandey and Kim, 2011). This review focuses on HDO catalysts, HDO mechanism, and kinetics study for catalytic HDO of lignin-derived phenols, which will contribute to further study on production of biofuels and chemicals by HDO of pyrolysis oils.

2. Pyrolysis oil

2.1. Properties of pyrolysis oils

The pyrolysis oil also called bio-oils is a dark brown, free flowing with smoky odor liquid from biomass pyrolysis (Massoth et al., 2006; Lu et al., 2009). The physical properties of bio-oil show that the water content, oxygen and ash contents of pyrolysis oil are obviously higher than those in heavy petroleum fuel, and the higher heating value of pyrolysis oil is much lower than that of petroleum fuel.

The pyrolysis oils are complex mixtures of more than 300 compounds derived from the depolymerization and fragmentation reactions of cellulose, hemicellulose, and lignin. The major organic compounds are acids, alcohol, ether, ketone, aldehyde, phenol, ester, sugar, furan, and nitrogen compounds. The phenolics compositions (phenol, guaiacol and other substituted phenol compositions) are formed by decomposition of lignin, while the other oxygenates such as sugar and furan should be formed from the depolymerization of cellulose and hemicellulose of biomass. The esters, acids, alcohols, ketones, and aldehydes may be produced from decomposition of the miscellaneous small oxygenated molecules (Huber et al., 2006). As a result, the deleterious properties of high viscosity, thermal instability, and corrosiveness present many obstacles to the substitution of fossil derived fuels by bio oils (Zhang et al., 2007; Diebold, 2000; Brems et al., 2011).

2.2. Instability of bio-oils

The instability of bio-oils is the result of their negative chemical properties such as complex mixtures of chemical compounds and high oxygen content (Brems et al., 2011). As a result, the viscosity

of bio-oils will be increased during storage and a fast increase will be observed by heating. Couples of complex chemical reactions may take place during aging of bio-oils (Diebold, 2000). Lu et al. (2009) concluded that aldehydes were the most unstable components since they can react with lots of different chemical compositions, such as water, phenolics, alcohols, and protein. Eventually, the properties of bio-oils will be changed with such kind of aging reactions, and these types of repolymerization reactions increased the average molecular of bio-oils, the viscosity, and the water content (Lu et al., 2009; Mortensen et al., 2011). Oasmaa et al. (2003) reported that phase separation and gummy formation derived by pyrolytic lignin and char/coke formation at higher temperature were observed during aging reactions. Therefore, these unfavorable characteristics of bio-oils make them difficult to be used. Upgrading is necessary before biomass pyrolysis oils can be used as competitive substitutes of petroleum fuels and chemical feedstocks in chemical industry.

2.3. Lignin decomposition and conversion

Lignin is the second most important components of lignocellulosic biomass after cellulose, which is about 23–33% of the mass of softwoods and 16–25% of the mass of hardwoods (Mohan et al., 2006). The lignin is composed of three different precursors: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The guaiacol lignin which is derived from the polymerization of coniferyl phenylpropane unit is found predominately in softwoods materials. The sinapyl unit is in hardwoods higher than that in softwoods. The structure of lignin implicates that it can be considered as the sources of value-added chemicals such as phenolics (Pandey and Kim, 2011).

Lignin is the most heat-resistant component in the three major components of lignocellulosic biomass, and is typically decomposed in the temperature range of 280–500 °C. As a result, more residual char was produced during lignin pyrolysis than pyrolysis of cellulose. Phenols were yielded as the result of lignin pyrolysis through the cleavage of ether (mainly α or β -o-4 bonds) and C–C linkages (Chen et al., 2001; Mohan et al., 2006).

The originality of lignin is very abundant with the development of lignocelluloses-to-ethanol process, which makes use of cellulose and hemicellulose but leaves lignin as a waste (Pandey and Kim, 2011). Additionally, the conventional pulp and paper industries also generate a large amount of lignin. Lignin is mainly being used as a low-grade energy source in combustion (Huber et al., 2006). However, both the chemical structure and abundant originality of lignin suggest that it has great potential to be used as value-added chemical feedstocks such as phenolic compounds, and the application of these products in chemical industry such as synthesis of phenol formaldehyde resin and plastics (Kleinert and Barth, 2008; Pandey and Kim, 2011). Furthermore, with the global energy crisis and the global warming issues, attentions have been increasingly paid to making liquid fuels and chemicals like aromatics and phenols by thermal treatment of lignin via depolymerization and conversion in hydrogen environment (Chen et al., 2001; Kleinert and Barth, 2008). Most studies on lignin decomposition and conversion have been simplified using lignin model compounds such as monomeric, dimeric, and trimeric model compounds (Pandey and Kim, 2011; Chen et al., 2001).

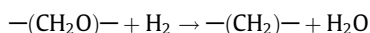
3. Biomass pyrolysis oils upgrading

In order to overcome the deleterious properties of the biomass pyrolysis oil, the upgrading process is required before its application. Currently, there are two major routes to make bio-oils being upgraded into a liquid transportation fuel: (1) catalytic

hydrodeoxygenation (HDO) (Furimsky, 2000), and (2) zeolite upgrading. The bio-oils upgrading is a complex reaction network due to the complex compositions of pyrolysis oils (Adjaye and Bakhshi, 1995; Mortensen et al., 2011). For these two routes, cracking, hydrocracking, hydrodeoxygenation, decarboxylation, decarbonylation, and hydrogenation have been reported to occur (Mortensen et al., 2011). The degree of deoxygenation and cracking of non-volatile components are the rate determining steps in bio-oil upgrading (Adjaye and Bakhshi, 1995).

3.1. Catalytic hydrodeoxygenation (HDO)

HDO of bio-oil involves the presence of catalyst and hydrogen at moderate temperature (300–600 °C). The oxygen is removed in the form of water. The overall reaction stoichiometry of HDO may be schematically represented by (Mahfud et al., 2007):



where $-(\text{CH}_2\text{O})-$ represents the carbohydrate in the bio-oil

The reactions may take place during catalytic HDO process including (Mortensen et al., 2011; Wildschut et al., 2009): (1) water separation; (2) dehydration reaction due to the condensation polymerization reactions; (3) decarboxylation reaction in which oxygen is removed as the form of H_2O ; (4) hydrogenation reaction which may involve the saturation of unsaturated components; (5) hydrogenolysis reaction which is related to the breakup of C–O bonds where the oxygen may be released in the form of water; and (6) hydrocracking reaction involving the breakdown of high molecular components into smaller molecules.

3.1.1. Two-stage hydrotreatment process

Elliott and Neuenschwander (1996) first proposed the two-stage hydrotreatment process. This process was performed in a down-flow (trickle bed) configuration consisting two fixed bed reactors at 21 MPa. The first reactor was operated below 300 °C as the low-temperature stabilization reactor. A subsequent main hydrodeoxygenation occurred in the second reactor at higher temperature (300–400 °C). The catalysts used were NiMo on γ -alumina and CoMo on spinel that were presulfided in the reactor before feeding the bio-oil. Furimsky (2000) pointed out that similar to the upgrading of the coal-derived liquids (CDLs) which have more than one stage required to obtain complete HDO because of the high content of oxygenates and aromatics, a two stage operation is beneficial for conversion biomass pyrolysis oil to quality competitive transportation fuels. The first stage is performed at temperature below 300 °C with sulfided CoMo or NiMo catalyst to remove O-compound and produce a stabilized oil product (Elliott, 2007; Furimsky, 2000). The second stage operated at the conditions of about 350 °C and 13.8 MPa. In the second stage, furans and phenols are the predominant oxygen compounds; because of the low HDO reactivity of these compounds, a higher reaction temperature and higher H_2 pressure are required to convert them into oxygen free products (Furimsky, 2000). However, the catalyst life of this process is poor due to breakdown of supports.

3.2. HDO catalysts

Table 1 shows the overview of catalysts for HDO of different model compound feeds. Industrial hydrodesulfurization (HDS) catalysts (e.g. Co–Mo or Ni–Mo Al_2O_3) which are used for removal of sulfur, nitrogen, and oxygen from petroleum fuels are utilized as HDO catalysts (Huber et al., 2006; Zhang et al., 2007; Mortensen et al., 2011). Most of HDO research work was done using Co–MoS₂ and Ni–MoS₂ as catalysts (Furimsky, 2000; Weigold, 1982; Bui et al., 2011a,b; Massoth et al., 2006; Wildschut et al., 2009). For these traditional HDS catalysts, Co and Ni serve as promoters

which donate electrons to the active sites – Molybdenum. Mortensen et al. proposed that this contributed to weaken the bond between molybdenum and sulfur so that a sulfur vacancy site is generated, and these sites are the active sites for both HDS and HDO. However, unsulfided form of the catalyst showed less activity than the sulfided catalysts (Wildschut et al., 2009), which indicates that the addition of a sulfur source will be beneficial for these catalysts.

Recently, some transition metal based catalysts including noble metals such as Pt, Pd and Ru and carbon based catalysts are utilized by some researches (Wildschut et al., 2009; Venderbosch et al., 2010; Zhao et al., 2011; Gutierrez et al., 2009; Centeno et al., 1999). Wildschut et al. investigated the effects of the noble-metal catalysts Ru/C, Pt/C, Pd/C on HDO of bio-oils in a batch reactor under a two stage operating conditions, mild HDO at 250 °C and 100 bar and deep HDO at 350 °C and 200 bar. The results showed that both the yields and the degree of deoxygenation were higher for the noble-metal catalysts than those for the traditional CoMo/ Al_2O_3 and NiMo/ Al_2O_3 catalysts. According to the combinations of oil yields, levels of deoxygenation and the extent of hydrogen consumption, they proposed that Ru/C might be the most promising catalyst for further study of catalytic HDO. Mortensen et al. (2011) pointed out that the transition metal catalysts should be bifunctional based on the mechanistic speculations. However, whether the activation of oxy-compound is achieved through the metal sites or at the metal support interface is still unclear though generally agreed that the metals contain the hydrogenation active sites (Mortensen et al., 2011). There are still some problems relevant to deactivation of catalysts led by coking and metal decomposition (Furimsky and Massoth, 1999). During catalytic HDO using traditional HDS catalysts, Al_2O_3 shown to be unsuitable support because the water formed in HDO and the oxygen containing compounds may convert it to boehmite ($\text{AlO}(\text{OH})$) (Mortensen et al., 2011; Elliott, 2007; Venderbosch et al., 2010). Observations showed that an indication of high affinity for carbon formation existed on the alumina support because of the relatively high acidity of Al_2O_3 (Popov et al., 2010). As a result, carbon has been found to be a promising alternative to Al_2O_3 due to its neutral nature and high surface area (Mortensen et al., 2011; Wildschut et al., 2009).

3.3. Deactivation of HDO catalysts

Furimsky and Massoth (1999) pointed out that there are three stages for catalyst deactivation: initial deactivation caused by coke; metal deposition; and pore constriction and ultimate pore blockage. It is known that coking is one of the major challenges for HDO reaction; and coking has close relationship with the structure of catalyst (Netzel et al., 1996) since polymerization reactions which are the major reactions leading to coking occur on the catalyst surface, which significantly reduces the active sites by competition with the reactant. As a result, the properties of the adsorbed feed have an important effect on coke formation. For the feeds with high content of coke precursors, Laurent et al. (1994) demonstrated that some phenols are important coke precursors, such as methoxy-phenol, hydroxyphenol, phenol or methylanisol, the pre-treatment of the catalyst is necessary (Furimsky and Massoth, 1999).

Furimsky and Massoth illustrated that besides feed composition and catalyst properties, the severity of conditions is another important factor that affects the extent of coke formation, such as hydrogen pressure, reaction temperature and contact time. Gualda and Kasztelan (1996) found that the coking extent decreased with the increase of hydrogen pressure, reaction temperature and contact time, which was the result of removal of coke precursors and an improved hydrogenation of the coke that deposited on the catalyst surface. Therefore, the design of active and stable HDO catalysts

Table 1

Overview of catalysts used for HDO of model compound.

Feed	Set-up	Catalyst	Support	T (°C)	P (MPa)	References
o-, m-, p-Cresols	Batch	CoMo/Al ₂ O ₃	Al ₂ O ₃	360	7	Wandas et al., 1996
Phenol	Batch	NiMo/Al ₂ O ₃	Al ₂ O ₃	350	7.5	Ryymin et al., 2010
4-Methyl-acetophenol, ethyldecanoate, guaiacol	Batch	CoMo/C	C	280	7	Puente et al., 1999
Guaiacol	Batch	Pt/ZrO ₂ , RhPt/ZrO ₂	ZrO ₂	350	1	Gutierrez et al., 2008
Phenol	Continuous	NiW/C	C	250–300	1.5	Echeandia et al., 2010
Pyrolysis oil	Batch	Noble metal	C, TiO ₂	250–350	10–20	Wildschut et al., 2009
Pyrolysis oil	Batch	Ru/C	C	350	20	Yoosuk et al., 2012
Phenol	Batch	Amorphous NiMoS		350	2.8	Odebunmi and Ollis, 1983
Cresol	Batch	CoMo/Al ₂ O ₃	Al ₂ O ₃	375–400	6.9	Yang et al., 2009
Methyl-phenols	Continuous	CoMo/Al ₂ O ₃	Al ₂ O ₃	300	2.85	Massoth et al., 2006
Phenol	Batch	CoMo/MgO, CoMoP/MgO	MgO	300–450	5	Ahmad et al., 2010
Guaiacol, cresols	Continuous	Pt/ZSM-5/, Pt/Al ₂ O ₃	ZSM-5, Al ₂ O ₃	200	4	Wang et al., 2012

that can be used with minimum hydrogen consumption and mild reaction condition is still a big challenge.

4. Mechanism of HDO of phenols

Due to the complex compositions of bio crude oils, most of the HDO studies reported have been focused on using model compounds rather than the real bio crude oils. Phenols have been received considerable attentions because of their low reactivity in HDO process. Therefore, the HDO of phenols becomes one of the key reactions in pyrolysis oil upgrading. A large portion of the work have been carried out to avoid the rings becoming saturated so as to minimizing the hydrogen consumption in HDO of model compound using phenols (Weigold, 1982; Bui et al., 2011a,b; Ahmad et al., 2010; Sepulveda et al., 2011). Apart from minimizing the hydrogen consumption by retaining the aromatic character of the upgraded oils, the unsaturated aromatics have a much higher octane value comparing with the saturated cyclic hydrocarbons (Elliott, 2007). Senol (2009) reported that two reaction routes were observed during HDO of phenol: (a) the aromatic ring has been retained and the C_{Arom}–O bond is hydrogenolysed; and (b) the aromatic ring is hydrogenated to be saturated before cleavage of the carbon-oxygen bond. Baker and Elliott (1993) developed a multi-step process in which the initial hydrotreating for oxygen reduction process was followed by separation of different components; and a second operation was designed for hydrocracking the heavy components. The two-step operation was possible to maximize the aromatics by removing the aromatic fraction before it became saturated; moreover, the hydrogen consumption was minimized by retaining the aromatic character.

Most phenols can be divided into two types in pyrolysis oils: the substituted phenols with alkyl such as cresol, and methoxyl such as guaiacol. Therefore, most of the attentions have been paid to study the HDO of alkyl substituted phenols and HDO of guaiacol as the model compounds (Odebunmi and Ollis, 1983; Bui et al., 2011a,b).

4.1. HDO of alkyl phenols

Odebunmi and Ollis (1983) investigated the HDO of cresols using sulphided CoMo/Al₂O₃ catalysts at low temperatures ranging from 220 to 270 °C and high temperatures in the range of 350–400 °C. The order of HDO reactivity for substituted phenols was: meta > para > ortho; this should have close relationship with the steric effect of o-substitution of phenols (Furimsky, 2000). Results revealed that toluene and cyclohexane were the main products. Subsequently, Wandas et al. (1996) investigated the conversion of cresols in the presence of sulfide CoMo catalyst in a stirred autoclave at the temperature of 360 °C and hydrogen pressure of 7 MPa. They observed that the highest conversion was obtained for

p-cresol, the o-cresol was least effective, methyl cyclohexane was the main product, toluene was the second main product, and the toluene yield for m-cresol and o-cresol was 27 and 11 mol.%, respectively. The main products distribution and total conversion of cresols were shown in Fig. 1. These results were in good agreement with results from Odebunmi and Ollis (1983), which also implied that the reaction of ring saturation was prior to the oxygen removal in the presence of CoMo/Al₂O₃ catalyst. Otherwise, toluene would be the main product as the direct deoxygenation (DDO) reaction was predominant.

In general, there are two parallel pathways for HDO of alkyl substituted phenols: direct deoxygenation (DDO) with the aromatic character retained and hydrogenation (HYD) with the aromatic ring being hydrogenated to be saturated. Massoth et al. (2006) carried out the catalytic HDO of methyl-substituted phenols in a flow microreactor at 300 °C and 2.85 MPa hydrogen pressure in the presence of sulfide CoMo/Al₂O₃. The observed primary reaction products include methyl-substituted benzene, cyclohexene, cyclohexane and H₂O. Their results analysis suggested two paths for HDO of phenols, the aromatics path and partially or completely cyclohexanes path, which is consistent with Odebunmi and Ollis' conclusions (Odebunmi and Ollis, 1983).

Yang et al. (2009) investigated HDO of phenol in supercritical hexane at different temperature range (300–450 °C) and 5.0 MPa of hydrogen pressure with sulfide CoMo and CoMoP catalysts supported on MgO. The results indicated that the CoMoP/MgO catalyst showed superior activating in HDO of phenol; the highest yield of benzene was obtained at 450 °C and reaction time of 60 min using CoMoP/MgO catalyst. The obtained products yields distribution reveals that the HDO activity of this catalyst increased drastically with the increase of the reaction temperature.

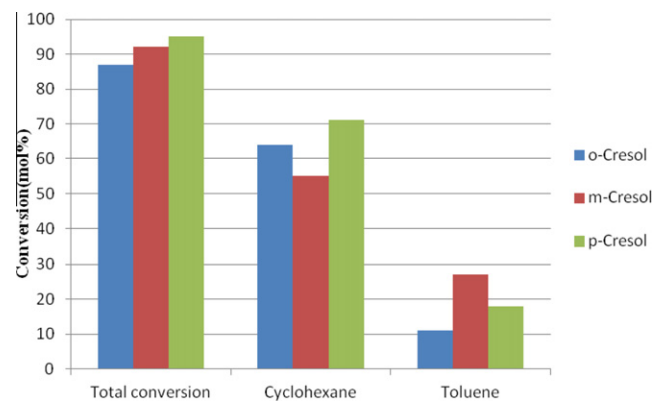


Fig. 1. Total conversion and main products yield distribution of cresol as model compound (360 °C, 7 MPa, 60 min). The figure is drawn based on data from Wandas et al. (1996).

Weigold (1982) carried out the direct HDO (C–O bond scission but the aromatic character retained) of ring alkyl-substituted phenols at temperature of 400 °C and 7.6 MPa hydrogen pressure in the presence of a commercial CoMo/Al₂O₃. The results indicated that the catalytically active site is stereochemically demanding in the HDO of phenols. He pointed out that the DDO and HYD reaction proceed on the same catalytic site and the DDO path was retarded mainly if the transfer of the substrate hydroxyl group onto a coordinatively unsaturated metal site of the catalyst has been inhibited.

4.2. HDO of methoxyl-substituted phenols

Other significant substituted phenols of pyrolysis oil are methoxyl-substituted phenols such as guaiacol (GUA). Studies on catalytic HDO of guaiacol as model compound of bio-crude have received increasing attention in the past. Bui et al. compared the effects of unsupported and alumina supported MoS₂ and CoMoS catalysts on HDO of GUA at temperature of 300 °C and 4 MPa hydrogen pressure (Bui et al., 2011a). The results verified that the DDO pathway for GUA conversion was obviously increased with the CoMoS catalyst compared to the non-promoted MoS₂ catalyst and this effect is similar to hydrodesulfurization (HDS) process. In a continuous study, Bui et al. studied the support effect for CoMoS catalysts in HDO of GUA (Bui et al., 2011b). Three different supports, Al₂O₃, TiO₂, ZrO₂, were tested to investigate the support effect of CoMoS catalysts on the selectivity and HDO activity of GUA. The effects of supports on selectivity in respect to GUA conversion revealed that there were slightly different for the primary products of transformation depending on different supports, for example, for CoMoS/Al₂O₃, catechol (CAT) and phenol were formed at low conversion rates; only CAT formed at low conversion rates on CoMoS/TiO₂; however, phenol was the main product for all different GUA conversion on CoMoS/ZrO₂. Besides, it was observed that the benzene yield was much higher on ZrO₂ supported catalyst compared with other two different supported catalysts. There are two parallel reaction pathways for GUA conversion: one is that phenol can be obtained directly with the effects of demethoxylation (DMO) of GUA; another one is demethylation (DME) in which catechol is produced as an intermediate, and then under the performance of methyl substitution and dehydration, phenol and alkyl substituted phenols are generated (Bui et al., 2011a,b). Li et al. (2011) pointed out that the similar mechanism for GUA conversion might be applicable when they investigated the influence of phenols on bio-oil upgrading over Pt/Al₂(SiO₃)₃, Pt/C or Pt/MgO catalyst.

Ahmad et al. (2010) investigated the possible routes and developed the feasible process route for upgrading of bio-oil into value-added transportation fuel via HDO process by simulation in PETRONAS iCON software. They proposed a three-stage process for upgrading of bio-oil via HDO by using GUA as model compound. The first stage consists of the conversion of GUA to catechol (CAT) by hydrogenolysis; the second stage involves hydrotreating of CAT to phenol; and the third stage is also called the stabilization stage by which value-added hydrocarbon such as benzene, cyclohexane and cyclohexene formed from the HDO of phenol. The results indicated that the selection of model compounds was a significant challenge for bio-oil upgrading and this simulation implicated the feasibility of HDO using model compounds to produce value-added transportation fuels. However, there are some disadvantages related to model limitations such as the complexity of the simulation due to the selection of feed phases and operation parameters and the designated unit operation.

Gutierrez et al. (2009) discussed the HDO of GUA as pyrolysis oil model compound using zirconia-supported noble metal catalysts. They observed that temperatures higher than 300 °C are required for HDO of GUA, which was in good agreement with the results

reported by Yang et al. (2009). The noble metal catalysts have potential to be a promising alternative to traditional sulfide catalysts due to the low carbon deposition on the noble metal catalysts. However, the low cost HDO catalysts should be the target of any further studies on HDO of bio-oils.

5. Kinetics of HDO of phenols

Bio-oil upgrading involves a complex combinations of parallel and series reactions in which the reaction constants and other parameters vary according to the operating conditions, for example, apparent activation energy values indicate that bio-oil is particularly sensitive to reaction temperature (Adjaye and Bakhshi, 1995). The kinetics of HDO has been investigated to better understand the HDO mechanism of pyrolysis oil. However, sparse reliable kinetic information of HDO of pyrolysis oil is reported due to the diversity of complex compositions of bio-oils, instead a variety of studies explored the HDO kinetics of different model compounds which were found to be the significant compositions of bio-oils with lower reactivity, such as phenols, furans, aldehydes (Massoth et al., 2006; Zhao et al., 2011; Odebunmi and Ollis, 1983; Sitthisa et al., 2011; Prochazkova et al., 2007). The experimental conditions used, such as catalyst, types of reactors, method of analysis, will have influence on the kinetic parameters obtained by different studies (Furimsky, 2000).

The kinetics of HDO of phenol and substituted phenols (used as model compound of bio-oils) have received increasing attentions in the past years since the existence of phenols in pyrolysis oil significantly affect the results of hydroprocessing of pyrolysis oil because of their low reactivity and the abundant originalities of lignin-derived phenols. Furimsky pointed out that most kinetics studies of HDO of phenols were performed in trickle bed reactors and batch reactors. The commercial sulphided CoMo and NiMo catalysts were favorable used catalysts (Furimsky, 2000).

Odebunmi and Ollis (1983) carried out a study on catalytic HDO of m-cresol in a packed bed trickle reactor over CoMo HDS catalysts. A Langmuir-Hinshelwood kinetic model is developed to illustrate the data:

$$F_c \frac{dX_c}{dW} = \frac{k_{HDO} K_H K_C C_C P_H}{(1 + K_C C_C + K_W C_W + K_S C_S)}$$

(HDO of m-cresol in a cresol-only feed) (S = mercaptan, W = water, c = cresol and H = hydrogen)

On the basis of the assumptions ($K_W C_W$ is neglected since water inhibition was found not to be significant; $K_H P_H$ (constant) is incorporated into k_{HDO}), the alternative expression of this equation is:

$$\begin{aligned} \frac{W}{F_{co}} &= - \left[\frac{1 + k_c C_{co}}{k_{HDO} K_c C_{co}} \right] \ln(1 - X_c) \\ &= - \frac{1}{k'_{HDO} C_{co}} \ln(1 - X_c) \end{aligned}$$

The HDO of m-cresol shows apparent first-order dependence on m-cresol concentration both in m-cresol-only and the mixed feed as shown in Table 2. Li et al. (1985) addressed the hydrodeoxygenation of phenolic compounds in the acid fractions over a sulfided

Table 2
The rate equation parameters for CRE (Odebunmi and Ollis, 1983).

Temperature (°C)	–lnk _{HDO}	K _c (CRE) (L/mol)
375	6.662	8.42
400	6.079	6.2
E _a (kcal/mol)	20.2	ΔH _c = kcal/mol
–lnA	9.0	ΔH _c = –11 kcal/mol

Ni–Mo/Al₂O₃ catalyst at 350 °C and 120 atm. The first-order kinetics for the overall conversion of phenolic compounds shows well for the HDO process. The pseudo-first-order rate constants indicate that the rate constants for each of the compound are almost the same (about 10^{−4} L/(g of cat. s)). The authors claimed that the HYD of phenolic compounds is faster than direct HDO under partial conditions though the data were not sufficient to demonstrate the competitive inhibition effects in these hydroprocessing reactions.

Laurent and Delmon (1993) studied the influence of competitors on activity and selectivity of HDO of phenols over sulfide Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ catalysts in a batch reactor at 350 °C and 7 MPa of hydrogen pressure. The results showed that the conversion of model compound (4-methylphenol (4MP)) follows apparent-first-order kinetics in this process. The pseudo-first-order rate constants used by Gevert et al. (1987) are used in this study:

$$-\ln\left(\frac{C_i}{C_0}\right) = k_{4MP} W f\left(\frac{t}{V}\right)$$

$$f\left(\frac{t}{V}\right) = \sum_{i=1}^n \frac{t_i - t_{i-1}}{V_{i-1}}$$

where C_i and C_0 are the concentrations of 4-methylphenol in samples i and 0; k_{4MP} is the apparent-first-order rate constant (cm³ min^{−1} g^{−1}); W is the catalyst weight (g); n is the number of samples taken; t is the time (min); and V is the solution volume (cm³).

The linear regression for the determination of the rate constants has demonstrated the validity of this equation. A Langmuir–Hinshelwood equation is used as kinetic expression of the inhibition:

$$\frac{k_{app}^0}{k_{app}} = 1 + K_i C_0$$

where k is the apparent-first-order rate constant without competitor in the feed, and k_{app} is the apparent-first-order rate constant at an initial competitor concentration C_0 . K_i is the inhibition constant presumed to represent the adsorption of the competitor on active sites.

The results demonstrate that there are two parallel reaction pathways for HDO of phenols: the direct hydrogenolysis of the C_{sp}–O bond (DDO), and the hydrogenation of the aromatic ring (HYD), which is in good agreement with literature reports (Bui et al., 2011a,b; Senol, 2009). The observations show that, in all cases, the hydrogenolysis path (DDO) is more inhibited than the hydrogenation path (HYD), which is consistent well with Li et al.'s (1985) conclusion that HYD of phenolic compounds is faster than direct HDO under partial conditions.

Massoth et al. (2006) discussed the correlations of kinetics parameters with molecular properties during catalytic HDO of methyl-substituted phenols. The Langmuir–Hinshelwood kinetics was used to analyze the obtained reaction data. Their observation also verified the presence of the two reaction pathway–HYD and C–OH (DDO). It is observed that the adsorption constant was found to be the same for both reaction paths, indicating that a single catalytic site center is operative for both reactions. They proposed that it was the substitutes' effects on the electrostatic potential and orbital rather than the steric effects that resulted in the dependencies of adsorption and reaction rates upon methyl substitution.

6. Overall aspects and prospect of catalytic HDO of lignin-derived phenols

Although a huge number of researches focused on catalytic HDO of lignin-derived phenolic compounds from biomass pyrolysis in

lab's perspective, further study to explore integration of existing oil refinery infrastructure for HDO of lignin-derived phenols in an industrial prospective is necessary. It is known that hydrogen consumption is one of the most significant factors that affect the cost of final products during HDO of bio-oils.

Currently, 96% of hydrogen used is produced from fossil fuels (Geantet and Guilhaume, 2008). However, considerable attentions have been paid to hydrogen production from biomass in the past years (Spath et al., 2005; Milne et al., 2002; Ni et al., 2006); for example, National Renewable Energy Laboratory (NREL) had developed two Aspen Plus models of hydrogen production via gasification; their preliminary screening study showed the potential of hydrogen to be an economic feasible product from biomass-derived syngas. In general, hydrogen can be produced from biomass by different routes, such as gasification, hydrogen from biomass-derived methanol and ethanol via steam reforming (Milne et al., 2002; Geantet and Guilhaume, 2008; Spath et al., 2005), and catalytic steam reforming of pyrolysis oil (Geantet and Guilhaume, 2008; Spath et al., 2005). Pyrolysis oil can be separated into two fractions according to water solubility; the oxygenated fraction or water-soluble fraction can be used for hydrogen production after water-insoluble fraction have been extracted for adhesive formulation (Ni et al., 2006; Wang et al., 1997). Marquovich et al. (1999) investigated hydrogen production from biomass by steam reforming of model compounds of pyrolysis oil with commercial nickel-based catalysts. They pointed out that the temperature played a significant role in the process; for example, the model compounds (acetic acid, m-cresol, and dibenzyl ether) were almost completely converted to hydrogen and carbon oxides with temperatures above 650 °C. However, carbonaceous deposits on catalyst for acetic acid were observed when temperatures were lower than 650 °C. Results suggest that it is difficult to reform sugars due to their rapid decomposition during the process and char forming in the reactor freeboard.

Geantet and Guilhaume (2008) summarized three possible reactions for catalytic production of hydrogen from bio-oils, including:

Steam reforming $C_xH_yO_z + (x-z)H_2O \rightarrow xCO + (x-z+y)H_2$; partial oxidation $C_xH_yO_z + (x-z)O_2 \rightarrow xCO + (\frac{y}{2})H_2$; and catalytic cracking. For catalysts used for hydrogen from biomass pyrolysis oil, Ni-based catalysts were favored in hydrogen production from biomass-derived pyrolysis oil (Milne et al., 2002; Ni et al., 2006; Wang et al., 1997). Milne et al. proposed the overall stoichiometry for catalytic steam reforming of bio-oil at 750–850 °C over a nickel-based catalyst, which gives a maximum yield of 17.2 g H/100 g bio-oil (Milne et al., 2002).

Wright et al. (2010) had developed two 2000 MT/day corn stover scenarios for bio-oil upgrading to transportation fuels: one is hydrogen generated from aqueous phase of bio-oil for fuel upgrading; another one is hydrogen purchased from an external source. Results show that the products value (PV) for hydrogen production scenario is \$3.09/gal of fuel which includes a bio-oil production cost of \$0.83/gal. Fuel yield for this scenario is 134 million liters of fuels per year. However, the PV is \$2.11/gal of fuels for the hydrogen purchase scenario of which the purchase price of hydrogen considered is \$1.5/kg. The fuel yield for this scenario is 220 million liters of fuels per year. The capital expenditures for hydrogen production and merchant hydrogen are estimated at \$287 million and \$200 million, respectively, indicating that the difference of PV between these two scenarios is derived by the high capital costs for hydrogen production due to additional equipment and installation costs. Besides, the low fuel yield which resulted from less bio-oil left for upgrading during hydrogen production scenario is another most significant factor that influences the PV. Sensitivity analysis suggested that an increase of fuel yields by slightly improved bio-oil upgrading processing will reduce the fuel cost

significantly; for example, a variation of 5% in the bio-oil upgrading will result in PV of \$2.60–3.89 for hydrogen production scenario (Wright et al., 2010). Undoubtedly, other factors, such as feedstock properties which may affect bio-oil quality and catalyst performance, will also impact the product yields and require further study.

UOP (Marker et al., 2005) hydrotreated dynamotive pyrolytic lignin and aimed to produce aromatics and gasoline. The obtained results suggest that pyrolytic lignin can be hydrotreated under mild conditions and further process and more active catalyst should be developed. The adiabatic pre-reforming technology was employed to integrate reforming of aqueous phase of bio-oil into an existing hydrogen plant for hydrogen production for upgrading of pyrolysis lignin phase. However, because of aqueous phase can account a large amount (~70%) of bio-oil weight, which only leaves a small amount (~30%) of bio-oils for upgrading and leads to the low yield of fuels. The original UOP analysis was modified by Wright et al.'s (2010) assumption that only a smaller fraction (38%) of bio-oil is needed to be reformed for providing hydrogen to upgrade the remaining bio-oil.

Marker et al. (2005) indicated that producing gasoline from pyrolytic lignin will become economically attractive at lower crude oil prices when pyrolysis oil price decreases. Furthermore, although the current fuel cost is lower for hydrogen purchase scenario, it is quite possible that the hydrogen selling price will have significant effect on fuel cost. Therefore, it still has great potential to explore cost effective hydrogen production scenario for bio-oil upgrading process. A summary of needs to achieve the goal for producing fuels from catalytic HDO of pyrolytic lignin-derived phase and general upgrading of bio-oil is as follows: (1) reduce capital cost for hydrogen production scenario by making use of the existing refinery units; (2) develop more active catalyst with good catalyst lifetime and investigate the limitations of reactors for scale up of bio-oil upgrading using existing refining units; (3) increase the yield of fuel by improvement of upgrading processing; and (4) further research is required to lower the high acid number of bio-oil which may lead to serious corrosion in standard refinery units.

7. Conclusions

Catalytic hydrodeoxygenation (HDO) of lignin-derived phenols which are the lowest reactive chemical compounds in pyrolysis oils has been reviewed. Catalysts having both high capabilities to avoid carbon formation and a sufficient activity for HDO are of a great challenge. The techno-economic analysis of catalytic HDO and bio-oil upgrading implies that further study on major technical and economic efforts are required to develop transportation fuel route from bio-oils, which include: (1) investigating improved catalysts; (2) exploring alternative hydrogen source; (3) detailed kinetics study; (4) optimizing the reaction conditions to make HDO of biomass derived phenols in the existing refinery infrastructure possible.

Acknowledgements

This work was supported in partial by the Office of Research and Department of Biological Systems Engineering at Washington State University.

References

Adjaye, J.D., Bakhshi, N.N., 1995. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways. *Fuel Processing Technology* 45, 185–202.

Ahmad, M.M., Nordin, M.F.R., Azizan, M.T., 2010. Upgrading of bio-oil into high-value hydrocarbons via hydrodeoxygenation. *American Journal of Applied Sciences* 7 (6), 746–755.

Baker, E.G., Elliott, D.C., 1993. Method of upgrading oils containing hydroxyaromatic hydrocarbon compounds to highly aromatic gasoline. US Patent, 5180868.

Brems, A., Dewil, R., Baeyens, J., Seville, J.P.K., Prayogo, C., Bending, G., 2011. The future of biomass pyrolysis in the production of value-added products. In: *Proceedings of the SDEWES Conference, Dubrovnik, September 26–29*.

Bridgwater, A.V., 1999. Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of Analytical and Applied Pyrolysis* 51, 3–22.

Bu, Q., Lei, H., Ren, S.J., Wang, L., Zhang, Q., Tang, J., Ruan, R., 2012. Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass. *Bioresource Technology* 108, 274–279.

Bui, V.N., Laurenti, D., Afanasiev, P., Geantet, C., 2011a. Hydrodeoxygenation of guaiacol with CoMo catalysts. Part I: Promoting effect of cobalt on HDO selectivity and activity. *Applied Catalysis B: Environmental* 101, 239–245.

Bui, V.N., Laurenti, D., Delichère, P., Geantet, Christophe, 2011b. Hydrodeoxygenation of guaiacol. Part II: Support effect for CoMoS catalysts on HDO activity and selectivity. *Applied Catalysis B: Environmental* 101, 246–255.

Buranov, A.U., Mazza, G., 2008. Lignin in straw of herbaceous crops. *Industrial Crops and Products* 28, 237–259.

Centeno, A., Maggi, R., Delmon, B., 1999. Use of noble metals in hydrodeoxygenation reactions. *Studies in Surface Science and Catalysis* 127, 77–84.

Chen, C.A., Pakdel, H., Roy, C., 2001. Production of monomeric phenols by thermochemical conversion of biomass: a review. *Bioresource Technology* 79, 277–299.

DeWild, P., VanderLaan, R., Kloekhorst, A., Heeres, H.J., 2009. Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation. *Environmental progress & Sustainable Energy* 28 (3), 461–469.

Diebold, J.P., 2000. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. NREL/SR-570-27613.

Echeandia, S., Arias, P.L., Barrio, V.L., Pawelec, B., Fierro, J.L.G., 2010. Synergy effect in the HDO of phenol over Ni–W catalysts supported on active carbon: effect of tungsten precursors. *Applied Catalysis B: Environmental* 101, 1–12.

Elliott, D.C., 2004. *Chemicals from Biomass*. Elsevier Inc., San Diego.

Elliott, D.C., 2007. Historical developments in hydroprocessing bio-oils. *Energy & Fuels* 21, 1792–1815.

Elliott, D.C., Neuenschwander, G.G., 1996. Liquid fuels by low-severity hydrotreating of biocrude. In: Bridgwater, A.V., Boocock, D.G.B. (Eds.), *Developments in Thermochemical Biomass Conversion*, vol. 1. Blackie Academic & Professional, London, pp. 611–621.

Freudenberg, K., Nash, A.C., 1969. Constitution and biosynthesis of lignin. *Science* 165, 784.

Furimsky, E., 2000. Catalytic hydrodeoxygenation. *Applied Catalysis A: General* 199, 147–190.

Furimsky, E., Massoth, F.E., 1999. Deactivation of hydroprocessing catalysts. *Catalysis Today* 52, 381–495.

Geantet, C., Guillaume, N., 2008. Hydrogen production from biomass. In: *Vanatrop 22–24 Oct 2008, Montpellier*.

Gevort, B.S., Otterstedt, J.E., Massoth, F.E., 1987. Kinetics of the HDO of methyl-substituted phenols. *Appl. Catal.* 31, 119–131.

Gualda, G., Kasztelan, S., 1996. Initial deactivation of residue hydrodemetallization catalysts. *Journal of Catalysis* 161, 319–337.

Gutierrez, A., Kailaa, R.K., Krause, A.O.I., 2008. Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on noble metal catalysts. (Extended Abstract). In: 14th ICC, Seoul, Korea.

Gutierrez, A., Kaila, R.K., Honkela, M.L., Slioor, R., Krause, A.O.I., 2009. Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catalysis Today* 147 (3–4), 239–246.

Huber, G.W., Iborra, S., Corma, A., 2006. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews* 106, 4044–4098.

Kleinert, M., Barth, T., 2008. Phenols from lignin. *Chemical Engineering and Technology* 31 (5), 736–745.

Kuroda, K., 2000. Analytical pyrolysis products derived from cinnamyl alcohol-end groups in lignins. *Journal of Analytical and Applied Pyrolysis* 53 (2), 123–134.

Laurent, E., Delmon, B., 1993. Influence of oxygen-, nitrogen-, and sulfur-containing compounds on the hydrodeoxygenation of phenols over sulfided CoMo/y-A1203 and NiMo/y-A1203 catalysts. *Industrial and Engineering Chemistry Research* 32, 2516–2524.

Laurent, E., Centeno, A., Delmon, B., 1994. Coke Formation during the Hydrotreating of Biomass Pyrolysis Oil: Influence of Guaiacol Compounds. *Catalyst Deactivation*, Elsevier, Amsterdam.

Li, C.L., Xu, Z., Gates, B.C., 1985. Catalytic hydroprocessing of SRC-II heavy distillate fractions. 4. Hydrodeoxygmatation of phenolic compounds in the acidic fractions. *Industrial and Engineering Chemistry Process Design and Development* 24, 92–97.

Li, W., Pan, C., Zhang, Q., Liu, Z., Peng, J., Chen, P., Lou, H., Zheng, X., 2011. Upgrading of low-boiling fraction of bio-oil in supercritical methanol and reaction network. *Bioresource Technology* 102, 4884–4889.

Lu, Q., Li, W.Z., Zhu, X.F., 2009. Overview of fuel properties of biomass fast pyrolysis oils. *Energy Conversion and Management* 50, 1376–1383.

Maher, K.D., Bressler, D.C., 2007. Pyrolysis of triglycerides for the production of renewable fuels and chemicals. *Bioresource Technology* 98, 2351–2368.

Mahfud, F.H., Ghijsen, F., Heeres, H.J., 2007. Hydrogenation of fast pyrolysis oil and model compounds in a two-phase aqueous organic system using homogeneous ruthenium catalysts. *Journal of Molecular Catalysis A: Chemical* 264, 227–236.

- Marker, T.L., Petri, J., Kalnes, T., McCall, M., Machowiak, D., Jerosky, B., Reagan, B., Nemeth, L., Krawczyk, M., Czernik, S., Elliot, D., Shonnard, D., 2005. Opportunities for biorenewables in oil refineries, final technical report. In: United States DOE/GO15085. UOP, Des Plaines, IL.
- Marquevich, M., Czernik, S., Chornet, E., Montane, D., 1999. Hydrogen from biomass: steam reforming of model compounds of fast-pyrolysis oil. *Energy & Fuels* 13, 1160–1166.
- Massoth, F.E., Politzer, P., Concha, M.C., Murray, J.S., Jakowski, J., Simons, J., 2006. Catalytic hydrodeoxygenation of methyl-substituted phenols: correlations of kinetic parameters with molecular properties. *Journal of Physical Chemistry B* 110, 14283–14291.
- Milne, T.A., Elam, C.C., Evans, R.J., 2002. Hydrogen from Biomass: State of the Art and Research, Challenges, IEA/H2/TR-02/001.
- Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & Fuels* 20, 848–889.
- Mortensen, P.M., Grunwaldt, J.D., Jensen, P.A., Knudsen, K.G., Jensen, A.D., 2011. A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General* 407, 1–19.
- Mukkamala, S., Wheeler, M.C., Heiningen, A.R.P., DeSisto, W.J., 2012. Formate-assisted fast pyrolysis of lignin. *Energy & Fuels*. <http://dx.doi.org/10.1021/ef201756a>.
- Netzel, D.A., Miknis, F.P., Mitzel, J.M., Zhang, T., Jacobs, P.D., Haynes Jr., H.W., 1996. Carbon-13 solid-state NMR investigation of coke deposits on spent catalysts used in coal liquefaction. *Fuel* 75, 1397–1405.
- Ni, M., Leung, D.Y.C., Leung, M.K.H., Sumathy, K., 2006. An overview of hydrogen production from biomass. *Fuel Processing Technology* 87, 461–472.
- Nigam, P.S., Singh, A., 2010. Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science* 37, 52–68.
- Oasmaa, A., Kuoppala, E., Solantausta, Y., 2003. Fast pyrolysis of forestry residue. 2. Physicochemical composition of product liquid. *Energy & Fuels* 17, 433–443.
- Odebunmi, E.O., Ollis, D.F., 1983. Catalytic hydrodeoxygenation. II: Interactions between catalytic hydrodeoxygenation of m-cresol and hydrodesulfurization of benzothiophene and dibenzothiophene. *Journal of Catalysis* 80, 65–75.
- Pandey, M.P., Kim, C.S., 2011. Lignin depolymerization and conversion: a review of thermochemical methods. *Chemical Engineering and Technology* 34 (1), 29–41.
- Popov, A., Kondratieva, E., Goupil, J.M., Mariey, L., Bazin, P., Gilson, J.P., 2010. Bio-oils hydrodeoxygenation: adsorption of phenolic molecules on oxidic catalyst supports. *Journal of Physical Chemistry C* 114, 15661–15670.
- Prochazkova, D., Zamostny, P., Bejblova, M., Cervený, L., Cejka, J., 2007. Hydrodeoxygenation of aldehydes catalyzed by supported palladium catalysts. *Applied Catalysis A: General* 332, 56–64.
- Puente, G., Gil, A., Pis, J.J., Grange, P., 1999. Effects of support surface chemistry in hydrodeoxygenation reactions over como/activated carbon sulfided catalysts. *Langmuir* 15, 5800–5806.
- Ren, S., Lei, H., Bu, Q., Wang, L., Chen, S., Wu, J., Ruan, R., 2012. Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. *Journal of Analytical and Applied Pyrolysis* 94, 163–169.
- Rocha, J.D., Luengo, C.A., Snape, C.E., 1996. Hydrodeoxygenation of oils from cellulose in single and two-stage hydrothermal pyrolysis. *Renewable Energy* 9, 950–953.
- Ryymin, E.M., Honkela, M.L., Viljava, T.R., Krause, A.Q.I., 2010. Competitive reactions and mechanisms in the simultaneous HDO of phenol and methyl heptanoate over sulphided NiMo/Al₂O₃. *Applied Catalysis A: General* 389, 114–121.
- Senol, O.I., 2009. Hydrodeoxygenation of aliphatic and aromatic oxygenates on sulphided catalysts for production of 2nd generation biofuels. Doctoral Thesis, Helsinki University of Technology, Finland.
- Sepulveda, C., Leiva, K., Garcia, R., Radovic, L.R., Ghampson, I.T., DeSisto, W.J., Fierro, J.L.G., Escalona, N., 2011. Hydrodeoxygenation of 2-methoxyphenol over Mo₂N catalysts supported on activated carbons. *Catalysis Today* 172 (1), 232–239.
- Sharma, R.K., Bakhshi, N.N., 1991. Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals. *The Canadian Journal of Chemical Engineering* 69 (5), 1071–1081.
- Sitthisa, S., Sooknoi, T., Ma, Y., Balbuena, P.B., Resasco, D.E., 2011. Kinetics and mechanism of hydrogenation of furfural on Cu/SiO₂ catalysts. *Journal of Catalysis* 277, 1–13.
- Spath, P., Aden, A., Eggeman, T., Ringer, M., Wallace, B. and Jechura, J., 2005. Biomass to hydrogen production detailed design and economics utilizing the battelle columbus laboratory indirectly-heated gasifier. Technical Report NREL/TP-510-37408.
- Tang, Z., Lu, Q., Zhang, Y., Zhu, X.F., Guo, Q.X., 2009. One step bio-oil upgrading through hydrotreatment, esterification, and cracking. *Industrial and Engineering Chemistry Research* 48, 6923–6929.
- Velden, M.V., Baeyens, J., Boukies, I., 2008. Modelling CFB biomass pyrolysis reactors. *Biomass and Bioenergy* 32, 128–139.
- Velden, M.V., Baeyens, J., Brems, A., Janssens, B., Dewil, R., 2010. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy* 35, 232–242.
- Venderbosch, R.H., Ardiyanti, A.R., Wildschut, J., Oasmaa, A., Heeres, H.J., 2010. Stabilization of biomass-derived pyrolysis oils. *Journal of Chemical Technology and Biotechnology* 85 (5), 674–686.
- Wandas, R., Surygata, J., Sliwka, E., 1996. Conversion of cresols and naphthalene in the hydroprocessing of three-component model mixtures simulating fast pyrolysis tars. *Fuel* 75, 687–694.
- Wang, D., Czernik, S., Montane, D., Mann, M., Chornet, E., 1997. Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. *Industrial and Engineering Chemistry Research* 36, 1507–1518.
- Wang, Y., He, T., Liu, K., Wu, J., Fang, Y., 2012. From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. *Bioresource Technology* 108, 280–284.
- Weigold, H., 1982. Behaviour of Co–Mo–Al₂O₃ catalysts in the hydrodeoxygenation of phenols. *Fuel* 61 (10), 1021–1026.
- White, J.E., Catallo, W.J., Legendre, B.J., 2011. Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies. *J. Anal. Appl. Pyrolysis* 91, 1–33.
- Wildschut, J., Mahfud, F.H., Venderbosch, R.H., Heeres, H.J., 2009. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Industrial and Engineering Chemistry Research* 48, 10324–10334.
- Wright, M.M., Satrio, J.A., Brown, R.C., Daugaard, D.E., Hsu, D.D., 2010. Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels. National Renewable Energy Laboratory, Golden, Colorado, USA.
- Yaman, S., 2004. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management* 45, 651–671.
- Yang, Y., Gilbert, A., Xu, C., 2009. Hydrodeoxygenation of bio-crude in supercritical hexane with sulfided CoMo and CoMoP catalysts supported on MgO: a model compound study using phenol. *Applied Catalysis A: General* 360, 242–249.
- Yoosuk, B., Tumnantong, D., Prasassarakich, P., 2012. Amorphous unsupported Ni–Mo sulfide prepared by one step hydrothermal method for phenol hydrodeoxygenation. *Fuel* 91, 246–252.
- Zhang, Q., Chang, J., Wang, T., Xu, Y., 2007. Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management* 48, 87–92.
- Zhao, C., He, J., Lemonidou, A.A., Li, X., Lercher, J.A., 2011. Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *Journal of Catalysis* 280, 8–16.